

AD-A114 393

ILLINOIS UNIV AT URBANA ROGER ADAMS LAB

F/G 7/4

THERMAL CHEMISTRY OF CYCLOPROPYL SUBSTITUTED MALONYL PEROXIDES.--ETC (11)

APR 82 M J DARMON; G B SCHUSTER

N00014-76-C-0745

NL

UNCLASSIFIED

TR-32

1 1
20-100

END
DATE
FILMED
6 82
DTIC

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

12

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N0014-76-C-0745-32	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Thermal Chemistry of Cyclopropyl Substituted Malonyl Peroxides. A New Chemiluminescent Reaction.		5. TYPE OF REPORT & PERIOD COVERED Technical
7. AUTHOR(s) Michael J. Darmon and Gary B. Schuster		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Illinois Urbana, IL 61801		8. CONTRACT OR GRANT NUMBER(s) N0014-76-0745
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Program, Materials Science Division Office of Naval Research, 800 N. Quincy Street Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-616
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE April 26, 1982
		13. NUMBER OF PAGES 33
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) chemiluminescence malonyl peroxides CIEEL thermolysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The thermal properties and chemiluminescent behavior of 4-cyclopropyl-4- methyl-1,2-dioxolane-3,5-dione (2) and 4-spiro[(2'-spirocyclopropyl)-cyclohexyl]- 1,2-dioxolane-3,5-dione were investigated. The gross chemical properties of these malonyl peroxides are analogous to other alkyl substituted examples. Ther- molysis leads to rate limiting homolytic rupture of the oxygen-oxygen bond, loss of CO ₂ and then cyclization to an α-lactone. This sequence of reactions can be catalyzed by aromatic hydrocarbons through an apparent electron transfer process.		

DTIC
ELECTE
MAY 12 1982
E

DTIC FILE COPY

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

82 05 12 021

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Chemiluminescence from these peroxides can be observed in the presence of the aromatic hydrocarbons. The mechanism for light generation is postulated to be chemically initiated electron-exchange luminescence (CIEEL) proceeding through a cyclopropylcarbinyl to allylcarbinyl rearrangement.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



OFFICE OF NAVAL RESEARCH

Contract N0014-76-C-0745

Task No. NR-051-616

TECHNICAL REPORT NO. N0014-76-C-0745-32

Thermal Chemistry of Cyclopropyl Substituted Malonyl Peroxides.

A New Chemiluminescent Reaction.

by

Michael J. Darmon and Gary B. Schuster

Prepared for Publication

in

Journal of Organic Chemistry

School of Chemical Sciences

University of Illinois

Urbana, Illinois 61801

April 26, 1982

Reproduction in whole or in part is permitted for

any purposes of the United States Government

Approved for Public Release; Distribution Unlimited.

Thermal Chemistry of Cyclopropyl
Substituted Malonyl Peroxides.
A New Chemiluminescent Reaction.

Michael J. Darmon and Gary B. Schuster*

Department of Chemistry
Roger Adams Laboratory
University of Illinois
Urbana, Illinois 61801

Thermal Chemistry of Cyclopropyl Substituted Malonyl Peroxides. A New
Chemiluminescent Reaction.

Document 105105
Abstract: The thermal properties and chemiluminescent behavior of 4-cyclopropyl-4-methyl-1,2-dioxolane-3,5-dione (2) and 4-spiro[(2'-spirocyclopropyl)-cyclohexyl]-1,2-dioxolane-3,5-dione were investigated. The gross chemical properties of these malonyl peroxides are analogous to other alkyl substituted examples. Thermolysis leads to rate limiting homolytic rupture of the oxygen-oxygen bond, loss of CO₂ and then cyclization to an α -lactone. This sequence of reactions can be catalyzed by aromatic hydrocarbons through an apparent electron transfer process. Chemiluminescence from these peroxides can be observed in the presence of the aromatic hydrocarbons. The mechanism for light generation is postulated to be chemically initiated electron-exchange luminescence (CIEEL) proceeding through a cyclopropylcarbiny to allylcarbiny rearrangement.

- 1 -

The reactions of organic peroxides that can produce visible light generally fall into two broad classes. The first is a unimolecular, concerted or stepwise, rearrangement of a high energy content molecule directly to an electronically excited state of a product. The second is the process we have recently described as chemically initiated electron-exchange luminescence (CIEEL).¹

The key elements of the CIEEL mechanism are electron transfer from some donor to the peroxide resulting in bond rupture and a rearrangement of the peroxide that, in essence, increases the reducing potential of the transferred electron. Next, an electron is given back to the donor generating its excited state which finally emits a photon of visible light.² In this sequence of reactions the peroxide plays several roles, and, therefore, there are important constraints on the structure of peroxides that will generate light efficiently by this path.

First, the peroxide must be easily reduced. It has been observed that peroxides containing adjacent carbonly groups are reduced at low potential.³ Thus diacyl peroxides are more easily reduced than peroxyesters which in turn are more easily reduced than dialkyl peroxides. Also, it has been our observation that cyclic peroxides are reduced more easily than their acyclic isomers. These considerations direct the search for new chemiluminescent molecules to cyclic diacyl peroxides.

Next, in order to produce light by the CIEEL process the reduced peroxide must undergo a rearrangement that generates a radical anion capable of a sufficiently energetic annihilation with the oxidized electron donor. For most of the examples of CIEEL so far reported this rearrangement involves splitting off a stable small molecule such as CO_2 . Also, it is widely held that the rearrangement must be very rapid so that it can compete successfully with back electron transfer from the peroxide to the donor.

To facilitate the investigation of the mechanism of light generation it is desirable that the peroxide be isolable so that its purity and concentration can be easily assessed. Several efficient chemiluminescent systems proceed through presumed unisolated peroxides. Among these are some of the most efficient light generators known such as the oxalate esters⁴ and luminol.⁵ However, because of uncertainties associated with the unisolated key peroxide the mechanism of light generation for these systems remains poorly defined.

Finally, if the chemiluminescent reaction is to have any practical significance, the peroxide should be relatively easy to prepare. These considerations led us to consider the possible generation of light by the CIEEL path from malonyl peroxides.

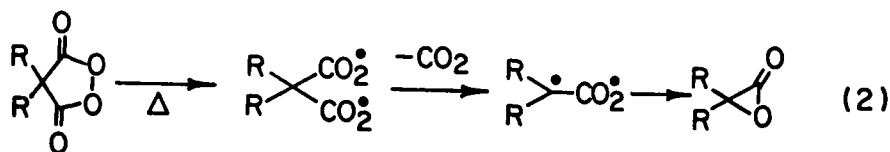
The preparation of a malonyl peroxide was reported first by Adam and Rucktäschel in 1971.⁶ Their synthesis is accomplished by treating the appropriate malonic acid with hydrogen peroxide in concentrated sulfuric acid. They observed that thermolysis or photolysis of di-n-butylmalonyl peroxide in an inert solvent results primarily in the formation of polymeric ester.⁷ They reasoned, and later confirmed by matrix isolation infrared spectrometry⁸, that the polymer arises from an intermediate α -lactone, eq. 1. The bis-trifluoromethyl



substituted α -lactone prepared from the appropriate peroxide was shown to be stable in dilute solution at low temperature.⁹

These observations led us to suspect that the first steps in the thermolysis of malonyl peroxides in inert solvent are the homolytic cleavage of the oxygen-oxygen bond followed by rapid decarboxylation to form a 1,3-biradical which closes to

generate the observed α -lactone, eq. 2. There is ample precedent for each of



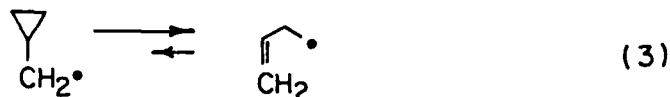
these steps.¹⁰ Whether two or more of these steps happen in concert is not known, and the examination of that question provides some of the motivation for the research reported herein.

A critical question surrounding the use of malonyl peroxides in chemiluminescent systems is the amount of energy released in their reaction. The heat of reaction for the transformation shown in eq. 2 is difficult to measure experimentally because of the instability of the α -lactone product. However, application of Benson's group equivalent method to the prototypical parent peroxide reveals a ΔH_r of ca. - 30 kcal/mole.¹¹ Thus, this reaction is probably not sufficiently exergonic to generate visible light, and no chemiluminescence from the thermolysis of a malonyl peroxide has been reported to date.

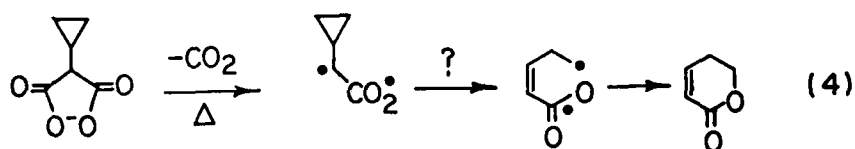
In typical chemiluminescent reactions of organic peroxides the bulk of the energy needed to produce a visible photon comes from conversion of the weak oxygen-oxygen bond of the peroxide to strong carbonyl bonds in the product. This feature is present in the thermal reactions of malonyl peroxide. However, in this case the formation of the strained α -lactone ring system greatly reduces the overall exothermicity of the transformation. It was our intention to construct malonyl peroxides substituted so that one of the suspected intermediates in eq. 2 could be diverted away from α -lactone toward a more exergonic path.

The cyclopropylcarbinyl-allylcarbinyl rearrangement (eq. 3) has been studied extensively.¹² This process, examined spectroscopically by Kochi,¹³ has been investigated by Ingold, Giller and coworkers¹⁴ who have measured the rate of reaction and Arrhenius activation parameters for several examples. This reaction

has been used as a "free-radical clock", and is one of the most rapid uni-



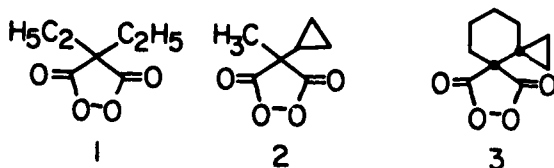
molecular rearrangements of an organic free radical yet discovered. Thus it appeared reasonable to us that substitution of a cyclopropyl group on the position between the carbonyl groups of malonyl peroxide would provide a second reaction pathway for the presumed biradical precursor to α -lactone, eq. 4.



Benson group equivalent calculations indicate that the transformation shown in eq. 4 is exothermic by ca. - 70 kcal/mole.¹¹ This reaction is therefore expected to be sufficiently exergonic to generate a photon of visible light. We set out to prepare appropriate cyclopropyl substituted malonyl peroxides and to examine their thermal and chemiluminescent properties. The results of that investigation are reported herein.

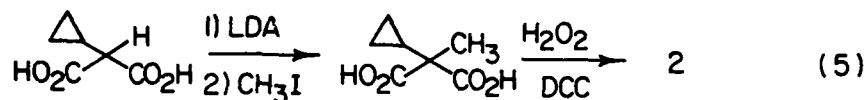
RESULTS

Synthesis: Malonyl peroxides 1, 2, and 3 were prepared to test the effect of cyclopropyl substitution on the thermal and chemiluminescent properties of this ring system.

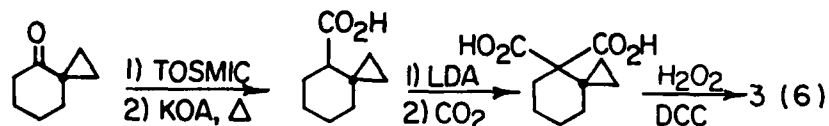


Preparation of peroxide 1 proceeds smoothly from diethylmalonic acid using the acid catalyzed cyclization procedure first introduced by Adam.⁷ The synthesis of cyclopropyl-methyl substituted peroxide 2 can be accomplished by methylation

of cyclopropylmalonic acid¹⁵ and then dicyclohexylcarbodiimide (DCC) mediated cyclization, eq. 5.¹⁶ The preparation of bis-spirocyclic peroxide **3** proceeds

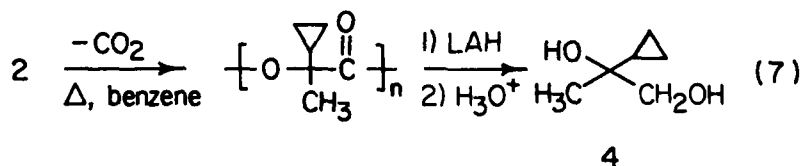


from spiro[5.2]octan-4-one¹⁷ through the malonic acid and then cyclization with DCC, eq. 6. The details of these reactions are presented in the Experimental Section.



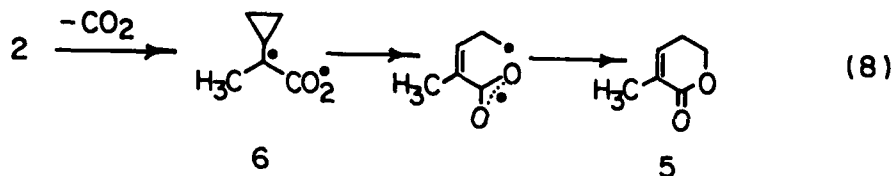
Thermal Reactions of Cyclopropyl-Substituted Malonyl Peroxides:

Thermolysis of peroxide **2** in nitrogen saturated benzene solution proceeds smoothly at reflux and gives a nearly quantitative yield of polymeric ester, eq. 7. The polyester was characterized by reduction with lithium aluminum hydride to diol **4**. By analogy with previous studies we conclude that the polymer



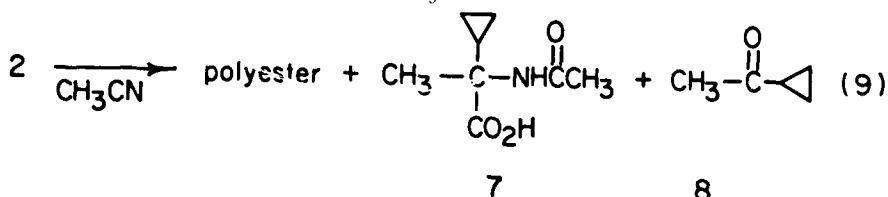
arises from the intermediate α -lactone.

If the hoped for cyclopropylcarbinyl-allylcarbinyl rearrangement takes place we expect the formation of lactone **5**, eq. 8. To examine this possibility we



prepared $\tilde{5}$ independently (see Experimental Section) and showed that it is stable to the reaction conditions. Analysis of the reaction mixture from $\tilde{2}$ under a variety of conditions by gas chromatography showed that less than 1% of $\tilde{5}$ is present. Evidently, the closure of the suspected biradical intermediate $\tilde{6}$ (eq. 8) to α -lactone occurs much more rapidly than the desired ring-opening rearrangement.

When the thermolysis of peroxide $\tilde{2}$ is carried out in dilute acetonitrile solution a different result is obtained. Polymeric ester is still formed but the major product is a crystalline white solid that we have identified as the amide substituted carboxylic acid $\tilde{7}$, eq. 9. Also, a small amount of methyl



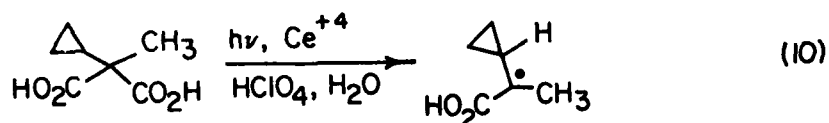
cyclopropyl ketone $\tilde{8}$ is formed under these conditions. Acid $\tilde{7}$ evidently results from the attack of acetonitrile solvent on the intermediate α -lactone, and ketone $\tilde{8}$ from the decarbonylation of this species.

The reactions of malonyl peroxides can be catalyzed with electron donors such as polynuclear aromatic hydrocarbons (*vide infra*). Under these conditions we expect that the intermediate of eq. 8 will be a radical anion rather than a biradical. Thermolysis of $\tilde{2}$ with perylene as catalyst in acetonitrile solution at 112° proceeds rapidly. The product of this reaction is predominantly the polymeric ester. Under these conditions acid $\tilde{7}$ is not formed presumably because the higher steady state concentration of α -lactone formed in the presence of catalyst polymerizes more rapidly than it adds solvent. No lactone $\tilde{5}$ could be detected from this reaction. It appears that the presumed radical anion intermediates also favors a path leading to α -lactone rather than opening of the cyclopropane ring. Thermolysis of spirocyclic peroxide $\tilde{3}$ leads to qualitatively similar results.

Electron Paramagnetic Resonance Spectroscopy:

Kochi and coworkers have reported the EPR spectra of several substituted cyclopropylcarbinyl radical systems at low temperature.¹³ They conclude, based on the magnitude of the coupling constants, that the plane of the carbinyl carbon bisects the cyclopropane ring. They also report that warming these radicals to ca. -100°C results in rearrangement to the corresponding allylcarbinyl radical.

We measured the EPR spectrum of the carboxylic acid substituted cyclopropylcarbinyl radical **9**. The radical was generated by photochemical oxidation of the malonic acid with $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ in HClO_4 according to the procedure of Greatorex and Kemp,¹⁸ eq. 10. The EPR spectrum of **9** at -140° showed a broadened



four line pattern centered at 2.0026 gauss. By computer simulation the coupling constants for the methyl hydrogens of 20.5 G and for the tertiary cyclopropyl hydrogen of 2.85 G are obtained. These coupling constants are essentially identical to those reported for the simple alkyl substituted cyclopropyl carbinyl radicals.^{13,14} This observation indicates that the geometry of **9** is the same as that of the substituted analogs.

Unlike the simple alkyl substituted radicals, warming the frozen solution of **9** did not result in rearrangement to the allylcarbinyl radical. The maximum temperature we could obtain was -80°, however, since above that temperature the EPR signal disappeared, presumably due to softening of the matrix and bimolecular reactions of the radical.

Kinetics of Thermal Decomposition:

The rate of the thermal reaction of the malonyl peroxides can be determined by any procedure that provides a reliable measure of the peroxide concentration.

We employed two methods to determine the rate of reaction. The first used infrared spectroscopy which followed the intensity of the peroxide carbonyl absorption. The second relied on the activated chemiluminescence from the peroxide which was shown to be directly proportional to the peroxide concentration. Both methods give the same results. This observation supports our conclusion that the malonyl peroxide is the source of the observed chemiluminescence (vide infra).

Since bis-spirocyclic peroxide 3 was the most efficient light generator of the malonyl peroxides that we examined, we concentrated most of our effort on this compound. However, to the extent we examined peroxide 2 its behavior was found to be exactly analogous to that of 3 .

Thermolysis of a dilute solution of peroxide 3 in benzonitrile containing 9,10-diphenylethynylanthracene (DPEA) as chemiluminescent activator gives light emission that decays in an approximately first-order fashion. When 1×10^{-2} M acetic acid is included in the reaction mixture the chemiluminescence intensity is decreased dramatically and the decay kinetics become cleanly first-order. Evidently, the acetic acid is reacting with an intermediate which is capable of going on to generate light and which also can react with the peroxide. This point will be examined further below.

The observed first-order decay of the chemiluminescence intensity yields a rate constant, k_{obs} . The magnitude of k_{obs} depends upon the concentration of DPEA, Figure 1, according to eq. 11, where k_1 is the rate constant for unimolecular reaction of peroxide 3 and k_{cat} is the rate constant for catalysis of

$$k_{\text{obs}} = k_1 + k_{\text{cat}}[\text{DPEA}] \quad (11)$$

DPEA. Extrapolation of the data shown in Figure 1 to $[\text{DPEA}] = 0$ gives k_1 while the slope of the line in Figure 1 gives k_{cat} . Both k_1 and k_{cat} are independent of the starting concentration of peroxide 3 and of the concentration of acetic acid. Also, other hydrocarbons capable of generating light from 3 give the

same k_1 but yield different values for k_{cat} . The rate data are summarized in Table 1. By monitoring the temperature dependence of k_1 and k_{cat} we are able to extract the activation parameters for these two processes.

The activation enthalpy for the unimolecular thermolysis of peroxide **3** (ΔH_1^\ddagger) in benzonitrile is 31.1 ± 2.3 kcal/mol and the activation entropy for this process (ΔS_1^\ddagger) is 3.8 ± 5.6 cal/mol.deg. These values are entirely consistent with unassisted homolysis of the oxygen-oxygen bond of the peroxide.¹⁹ And thus these activation parameters tend to confirm the assumed mechanism shown in eq. 2.

The activation enthalpy for the DPEA catalyzed reaction of peroxide **3** (ΔH_{cat}^\ddagger) is 15.6 ± 1.0 kcal/mol and the activation entropy for this process (ΔS_{cat}^\ddagger) is -17.6 ± 2.6 cal/mol.deg. These values point to efficient catalysis by DPEA through a transition state which is composed of one molecule of peroxide and one molecule of the hydrocarbon. The mechanism of the catalytic process is revealed by using different hydrocarbons as catalysts. The data in Table 1 show that the effectiveness of the hydrocarbon as a catalyst is strongly dependent on the structure of the hydrocarbon. A semilogarithmic plot of k_{cat} against the one electron oxidation potential of the hydrocarbon (E_{ox}) gives an excellent linear correlation indicative of rate-limiting electron transfer from the hydrocarbon to the peroxide.²⁰ The slope of this line is -18 ± 2 V⁻¹ which yields a transfer coefficient, α , of 0.64. This observation substantiates the notion stated earlier that cyclic diacyl peroxides, such as malonyl peroxide, are easily reduced by ground-state organic electron donors.

The total activation enthalpy of the reactions leading to the eventual generation of light in a chemiluminescent reaction (ΔH_{chl}^\ddagger) can be obtained by measuring the effect of temperature on the light output.²¹ Application of this technique to peroxide **3** and DPEA in benzonitrile, Figure 2, gives an ap-

parent ΔH_{chl}^\ddagger of 23.5 ± 1.0 kcal/mol. This value is approximately 8 kcal/mol greater than the activation enthalpy for the rate limiting step in the catalytic reaction of $\mathbf{3}$. This observation indicates that there is at least one additional step in the chemiluminescent reaction sequence with a significant activation energy. It is crucial to understand that only the peroxide molecules destined to give a photon of light need suffer the additional 8 kcal/mol activation enthalpy. The major part of the reaction is free to follow a lower energy path if one exists.

Chemiluminescence of Malonyl Peroxides:

The thermal decomposition of cyclopropyl substituted malonyl peroxides $\mathbf{2}$ and $\mathbf{3}$ in the presence of fluorescent aromatic hydrocarbons results in weak but easily detected chemiluminescence. The presence of the cyclopropyl group is an absolute requirement for light generation. Diethylmalonyl peroxide $\mathbf{1}$ does not give detectable light under any conditions we have explored. Also, spirocyclic peroxide $\mathbf{3}$ is ca. 30 times more effective at generating light than its bicyclic counterpart $\mathbf{2}$. For this reason we concentrated our investigation on the properties of peroxide $\mathbf{3}$.

Thermolysis of $\mathbf{3}$ in benzene or benzonitrile solution in the absence of a fluorescent hydrocarbon does not give any detectable light. This observation indicates that generation of an emissive electronically excited state from the unimolecular reactions of $\mathbf{3}$ is quite improbable. However, chemical light generation is easily detected when an aromatic hydrocarbons such as DPEA, 9,10-diphenylanthracene (DPA), or perylene is included with the peroxide. In all cases the chemiluminescence emission spectrum corresponds perfectly to the fluorescence spectrum of the added hydrocarbon. Significantly, when 9,10-dibromoanthracene (DBA) is included in peroxide $\mathbf{3}$ solutions the amount of light observed is more than 200 times lower than when DPA is used. This finding indicates that the chemiluminescence in the presence of the fluorescer is not

due to the direct formation of a non-emissive triplet excited state followed by a triplet-to-singlet energy transfer. If that were the case then DBA, after correction for different emission quantum yields, should generate light more efficiently than does DPA.²²

The process responsible for chemical light generation is revealed by examining the light producing effectiveness of various aromatic hydrocarbons. The chemiluminescent intensity can be measured under conditions where the concentration of peroxide is essentially constant. Comparison of the emission intensity at constant hydrocarbon concentration, corrected for different fluorescence quantum yields, gives the results shown in Figure 3. The slope of this line is $-17 \pm 2 \text{ V}^{-1}$ which is the same, within experimental error, as that obtained for the catalytic decomposition of the peroxide by these hydrocarbons. This finding indicates that the same process that is responsible for the catalysis of the peroxide decomposition is also responsible for light generation. That is, the efficiency of excited state generation is directly related to the ability of the aromatic hydrocarbon to act as a one electron donor. This observation is strong evidence in support of the operation of the CIEEL mechanism.

In all of the previously reported examples of CIEEL chemiluminescence the light generating path is remarkably insensitive to the presence of low concentrations of O_2 or protic solvents. This is not the case with peroxide 3. In particular, we find that O_2 , or low concentrations of acetic acid or methanol, are quite effective quenchers of the chemiluminescence. However, these substances do not change the rate at which the peroxide reacts. This observation indicates that these quenchers are intercepting an intermediate on the path to light generation that is formed after the rate limiting step of the reaction. The quenching by acetic acid and methanol was investigated quantitatively, Figure 4. The effectiveness of the quencher appears to be related to acid strength. Acetic acid gives k_{qT} of 2900 M^{-1} while methanol gives a slope of only 10 M^{-1} . Thus it seems that some species capable of being protonated plays a crucial role in the

chemiluminescence of these malonyl peroxides. Moreover, it is apparent that protonation of this species removes it from the path leading to the generation of light.

Discussion:

The results reported herein reveal information about the mechanism of thermal decomposition of malonyl peroxides, the rate of ring closure of 1,3-biradicals relative to the cyclopropylcarbinyl-allylcarbinyl rearrangement, and the mechanism for generation of light from the thermal reactions of organic peroxides.

Cleavage of the oxygen-oxygen bond of a peroxide is typically the initiating step in its thermal reaction. For diacyl peroxides this bond dissociation is sometimes coupled to rupture of the adjacent carbon-carbon bond to give CO_2 in one step. The activation parameters for reactions of these peroxides have been used as a guide to the degree of simultaneous two, or more, bond cleavage.¹⁹ Our results are entirely consistent with unassisted oxygen-oxygen bond homolysis as the rate limiting step in the reaction of malonyl peroxides.

The major products observed from the thermolysis of cyclopropyl substituted malonyl peroxides **2** and **3** apparently result from decarboxylation of the initially generated biradical to form the appropriate cyclopropylcarbinyl biradical. This biradical in principle can partition between ring closure to the α -lactone and opening of the cyclopropyl ring; the process we hoped to detect by ring expansion to the δ -lactone. Our inability to detect any of the ring expanded lactone shows that the rate of closure to the α -lactone is much faster than the cyclopropylcarbinyl-allylcarbinyl rearrangement for these molecules.

Chemiluminescence can be a more sensitive indicator of the reaction pathways than is the product study. Scheme 1 shows a path leading to light generation that is consistent with all the information that we have gathered about the reactions of these substituted malonyl peroxides.

The first step in the sequence is activated electron transfer from the aromatic hydrocarbon (activator, ACT) to the peroxide resulting in cleavage of the oxygen-oxygen bond, giving the malonate radical anion and the ac-

tivator radical cation. The next step is the rapid loss of CO_2 to generate the carboxylate substituted cyclopropylcarbinyl radical. This radical is presumably formed in the solvent cage with the activator radical cation. Back electron transfer within the solvent cage to generate eventually the α -lactone is apparently the predominant reaction path.

The light generation path must involve the cyclopropyl substituent since analogous alkyl substituted malonyl peroxides do not generate light. Scheme 1 shows our postulate that the ring opening of the cyclopropane leads to a δ -lactone radical anion that eventually is responsible for the chemiluminescence. If the difference in activation energy between the catalytic path and the light generating path of 8 kcal/mol corresponds to the partitioning between the ring opening and back electron transfer, then we estimate that the minor chemiluminescent path accounts for only ca. 0.002% of the reaction. This is well below our limit of detectability for products, but can easily account for all of the chemiluminescence that we detect. The difference between the chemiluminescence yield of peroxides 2 and 3 is accommodated by this mechanism as well. The rigidity of the spirocyclic system ensures the proper stereoelectronic arrangement for ring opening and formation of the δ -lactone.

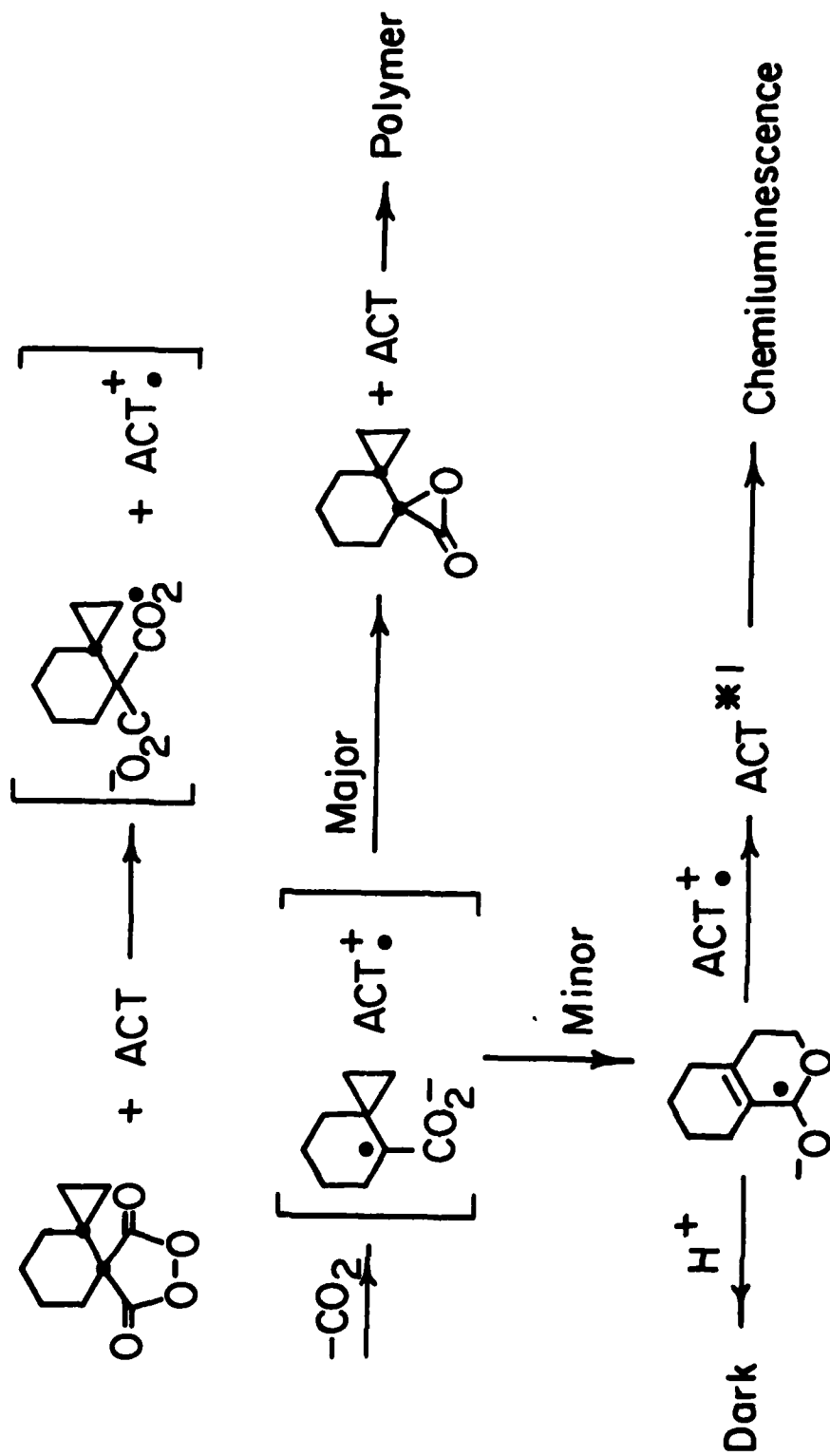
The postulated mechanism also accounts easily for the effect of protic substances on the chemiluminescence of these malonyl peroxides. Protonation of the ring expanded lactone, as shown in Scheme 1, removes the radical anion from the light generating path. The lactone radical anion should also easily reduce the starting malonyl peroxide in a chain reaction contributing to the non-first-order kinetic behavior observed in the absence of proton donors.

The penultimate step in the CIEEL light generating sequence is the annihilation of the oppositely charged radical ions. This process leads to generation of the excited activator which we detect by its luminescence.

In conclusion, the question asked at the outset of this research is ans-

wered in part. It is possible to harness the energy released in the decomposition of a malonyl peroxides substituted with a proximate cyclopropyl group and convert it to a photon of light. However, the efficiency of this process is very low. This appears to result from slow conversion of the cyclopropylcarbinyl radical to the allylcarbinyl radical compared to the rate of back electron transfer. We are continuing to investigate ways to decrease the activation barrier for the chemiluminescent path and thereby increase the yield of light from these reactions.

Scheme 1



Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian Associates EM-390, HR-220 or a Nicolet NT-360 spectrometer with tetramethylsilane as the internal standard. IR spectra were obtained with a Perkin-Elmer 137 sodium chloride or a 237B grating infrared spectrophotometer and a Nicolet 7199 FT-IR instrument. UV-VIS absorption spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Fluorescence spectra were recorded on a Farrand Mark I Spectrofluorometer or by photon counting to permit direct comparison with chemiluminescence emission spectra. EPR spectra were recorded on a Varian Associates E-4 (X-Band) Spectrometer. Gas chromatographic analyses were done on a Varian Aerograph 2700 or a Hewlett Packard 5790A gas chromatograph equipped with flame ionization detectors. Mass spectra were obtained with Varian MAT CH-5 and 731 mass spectrometers. Elemental analyses, active oxygen and molecular weight determinations were performed by the Analyses Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois. Melting points were obtained with a Büchi Schmelzpunktbestimmungsapparat and are uncorrected.

Chemiluminescence Measurements and Techniques. The photon-counting technique was used for all chemiluminescence measurements. An EMI 9813B photomultiplier tube was employed for detection of chemiluminescence. Spectral resolution was accomplished with a Jarrel-Ash 0.25m monochromator, equipped with a grating with 1180 grooves/mm. The bandpass under high resolution conditions is calculated to be 5 nm, and under low resolution conditions it is calculated to be 26 nm. The data were collected in a 128 channel digital input buffer with a variable time per channel of 1 to 800 seconds. The buffer was interfaced with a Digital Equipment Corporation VAX 11/780 which was used for all data analysis. The chemiluminescence sample temperature was regulated to within $\pm 0.1^\circ\text{C}$ by means of an electrically heated cell holder.

A one centimeter Pyrex cuvette equipped with a Teflon stopcock was used for all measurements. To obtain reproducible results all glassware used in the preparation of samples or used in the actual measurement of chemiluminescence was scrupulously cleaned. The following procedure was used to clean all glassware used for these purposes. The glassware was soaked in a solution of concentrated Nochromix (Godax Laboratories) in reagent grade sulfuric acid and then rinsed with deionized water, distilled in glass acetone (Burdick & Jackson), and purified benzene. It was then allowed to dry at room temperature. Once the glassware was cleaned by this method and shown to be free of contaminants by reproducible chemiluminescent results, it was cleaned between individual experiments by rinsing well with purified benzene. The solvent used for all chemiluminescence experiments was freshly distilled benzonitrile unless specifically stated otherwise.

4,4-Diethyl-1,2-dioxalane-3,5-dione (1). Peroxide 1 was prepared by the general method reported by Adam and Rucktäschel.^{6,7} Diethylmalonic acid (1.30 g, 8 mmol) in methanesulfonic acid (5 ml) was stirred at 25°C behind a safety shield while 90% H₂O₂ (1.0 ml) was added in portions over an hour. The reaction mixture was stirred at 25°C for an additional 24 h and the solution was poured onto crushed ice. Saturated ammonium sulfate was added and the cold aqueous mixture was extracted with pentane. The combined pentane extracts were washed with aqueous (NH₄)₂SO₄ (sat), aqueous NaHCO₃ (10%), and aqueous NaCl (sat). The pentane solution was dried with MgSO₄ and the solvent removed in vacuo. Distillation of the crude material at reduced pressure gave a colorless liquid (0.84 g, 65%): b.p. 45°C/3mm; ¹H NMR (CCl₄) δ 1.03 (t, 6H, CH₃), 1.97 (q, 4H, CH₂); IR (CCl₄) ν_{C=O} 1795 cm⁻¹.

Anal. Calcd for C₇H₁₀O₄: C, 53.16; H, 6.37; Active Oxygen, 10.12; Molecular Weight, 158. Found: C, 53.41; H, 6.52; Active Oxygen, 10.23; Molecular Weight (Osmometry), 160.

2-Methyl-2-cyclopropylmalonic acid. Under a dry nitrogen atmosphere 45 ml of n-BuLi (2.2 M in hexane) was slowly added to a stirred solution of cyclopropylmalonic acid (4.86 g, 30.8 mmol) in 150 ml of dry freshly distilled THF at -78°C . The reaction mixture was allowed to warm to 25°C , stirred for an additional hour and then cooled to -78°C . Methyl iodide (9.2 g, 64 mmol) was added and the contents of the flask was allowed to warm to 25°C . After stirring for an additional 2 h the solution was diluted with an equal volume of water and washed with Et_2O . The aqueous extract was acidified at 0°C with 10% HCl to pH 5-6 and extracted with Et_2O . The ether layer was washed with saturated NaCl, dried (MgSO_4), and the solvent removed in vacuo. The solid residue was recrystallized from nitromethane to yield 3.99 g (75%) of white crystals: mp $143-144^{\circ}\text{C}$ (gas evolution); ^1H NMR (acetone- d_6) δ 0.030-0.55 (m, 4H, cyclopropyl), 1.20 (s, 3H, CH_3), 1.30-1.70 (m, 1H); IR (Nujol) $\nu_{\text{C=O}}$ 1700 cm^{-1} .

Anal. Calcd for $\text{C}_7\text{H}_{10}\text{O}_4$: C, 53.16; H, 6.37. Found: C, 52.95; 6.32.

4-Cyclopropyl-4-methyl-1,2-dioxolane-3,5-dione (2). Cyclopropylmethyl malonic acid (1.83 g, 11.6 mmol) was dissolved in 8.75 mL of Et_2O and 3.75 mL of methanesulfonic acid and stirred at 25°C behind a safety shield. Hydrogen peroxide (2 mL, 90%) was slowly added in order to avoid heating of the reaction mixture. Six hours later an equal amount of hydrogen peroxide was added following the same precautions. The solution was stirred at 25°C for an additional 24 h and was worked up in the same way as described for peroxide 1. Distillation of the crude material at reduced pressure gave a colorless liquid (0.92 g, 51%): b.p. $43^{\circ}\text{C}/0.5\text{ mm}$; ^1H NMR (CCl_4) δ 0.56-0.76 (m, 4H, cyclopropyl), 1.13-1.50 (m, 1H), 1.60 (s, 3H, CH_3); IR (Film) $\nu_{\text{C=O}}$ 1800 cm^{-1} .

Anal. Calcd for $\text{C}_7\text{H}_8\text{O}_4$: C, 53.84; H, 5.16; Active Oxygen, 10.25; Molecular Weight 156. Found: C, 54.10; H, 5.12; Active Oxygen, 10.18; Molecular Weight (Osmometry), 163.

Peroxide 2 can be prepared by the alternate method of DCC and H_2O_2 which

is described in full detail for peroxide 3. The crude peroxide 2 that is prepared by this method is purified by reduced pressure distillation and all of its physical properties are identical to the material prepared by the acid catalyzed procedure.

4-Cyanospiro[5,2]octane. Under a nitrogen atmosphere and with rapid stirring with a mechanical stirrer, a solution of t-BuOK (12.3 g, 110 mmol) in 40 ml of dry DMSO was cooled to just above the freezing point of the solution. Solid tosylmethyl isocyanide (TOSMIC) (6.8 g, 35 mmol) was added all at once to the cold solution and allowed to stir for 5 min. Dry methanol (1.0 mL) and spiro[5.2]octan-4-one¹⁷ (3.0 g, 24 mmol) was added and stirred for 24 h at 25°C. The reaction mixture was diluted with H₂O, acidified at 0°C with 10% HCl to pH ~6, and extracted with petroleum ether. The combined organic extracts were washed with saturated NaCl solution, dried (Na₂SO₄) and passed through a short column of neutral alumina and the solvent removed in vacuo. Vacuum distillation gave a colorless liquid (2.3 g, 70%): b.p. 70-72°C/5mm; ¹H NMR (CCl₄) δ 0.30-0.70 (m, 4H, cyclopropyl), 1.00-2.00 (m, 8H, cyclohexyl), 2.30 (t, 1H, CHCN); IR (liquid) ν_{CN} 2260 cm⁻¹.

Anal. Calcd for C₉H₁₃N: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.68, H, 9.48; N, 10.13.

Spiro[5.2]octane-4-carboxylic Acid. A solution of 4-cyanospiro[5.2]octane 22.1 mmol, ethylene glycol (25 mL) and KOH (10.3 g) was heated at reflux until the evolution of ammonia ceased (approximately 48 h). The reaction mixture was allowed to cool, diluted with H₂O, and continuously extracted with Et₂O until all the ethylene glycol was removed. The aqueous portion was acidified to pH 5 with HCl and extracted with Et₂O. The organic layer was washed with saturated NaCl, dried (MgSO₄) and the solvent removed in vacuo. Vacuum distillation yielded a colorless liquid (2.59 g, 76%): b.p. 75°C/0.5 mm; ¹H NMR (CCl₄) δ 0.20-0.70 (m, 4H, cyclopropyl), 0.80-1.10 (m, 1H, cyclohexyl), 1.30-2.20 (m, 8H, cyclohexyl); IR (liquid) $\nu_{\text{C=O}}$ 1700 cm⁻¹.

Anal. Calcd for C₉H₁₄O₂: C, 70.10; H, 9.15. Found: C, 70.29; H, 9.31.

Spiro[5.2]octane-4,4-dicarboxylic Acid. Under a dry nitrogen atmosphere, lithium diisopropylamide (LDA) (11.4 mmol), 5 ml dry THF was slowly added to a stirred solution of spiro[5.2]octane-4-carboxylic acid (0.552 g, 3.6 mmol) in 10 ml of dry, freshly distilled THF at -78°C . The contents of the flask was allowed to warm to 25°C , stirred for an additional 2 h and cooled again to -78°C . A rapid stream of dry CO_2 was bubbled through the solution while the temperature of the solution was allowed to slowly rise to 25°C . The reaction mixture was diluted with Et_2O (100 mL) and extracted with H_2O (2x50 mL). The aqueous layer was acidified to pH 5 with HCl at 0°C and extracted with Et_2O (3x50 mL). The organic extract was washed with saturated NaCl, dried (MgSO_4), and the solvent removed in vacuo. The solid residue was recrystallized from nitromethane to yield 0.440 g (62%) of white crystals: mp $203\text{--}204^{\circ}\text{C}$ (gas evolution); ^1H NMR (DMSO-d_6) δ 0.20 (m, 2H, cyclopropyl), 0.50 (m, 2H, cyclopropyl), 1.40 (s, 6H, cyclohexyl), 1.90 (br.s., 2H, cyclohexyl); IR (Nujol) $\nu_{\text{C=O}}$ 1700 cm^{-1} .

Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4$: C, 60.59; H, 7.12. Found: C, 60.55; H, 7.17.

4-Spiro[2'-spirocyclopropyl]-cyclohexyl]-1,2-dioxolane-3,5-dione (3).

Spiro[5.2]octane-4,4-dicarboxylic acid (0.20 g, 1.0 mmol) dissolved in 8 mL $\text{Et}_2\text{O-CH}_2\text{Cl}_2$ (1:1) was added dropwise over 6 h to a mechanically stirred solution of dicyclohexylcarbodiimide (DCC) (0.60 g, 2.9 mmol), CH_2Cl_2 (2 mL) and H_2O_2 (2 mL, 3.5 M in Et_2O) maintained at 4°C . Oxalic acid (50 mg) was added to the cold reaction mixture 24 h after the final addition of H_2O_2 -DCC and stirred for an additional 15 min. The suspended urea and undissolved oxalic acid were removed by filtration through a sintered glass funnel and washed with pentane. The combined filtrate and pentane washings were washed with cold saturated $(\text{NH}_4)_2\text{SO}_4$, Na_2CO_3 (10%), and saturated NaCl. The organic layer was dried with MgSO_4 and the solvent removed in vacuo. The crude product was chromatographed on silica with 1% Et_2O in pentane at -20°C and then sublimed at 10^{-4} torr onto a dry-ice acetone cooled trap. Analytically pure material was obtained by repeating the cold-column procedure and the sublimation. This resulted in 35 mg (17%) of a white solid: mp $40\text{--}41^{\circ}\text{C}$; ^1H NMR (CCl_4) δ 0.33-0.83 (m, 4H, cyclopropyl), 1.53-

2.15 (m, 8H, cyclohexyl); IR (CCl₄) $\nu_{C=O}$ 1792.

Anal. Calcd for C₁₀H₁₂O₄: C, 61.22; H, 6.17; Active Oxygen, 8.15; Molecular Weight, 196. Found: C, 61.35; H, 6.05; Active Oxygen, 8.00; Molecular Weight (Osmometry), 204.

1-Oxa-3-methylcyclohex-3-ene-2-one. Under a dry nitrogen atmosphere, 5.0 mL of n-BuLi (2.4 M in hexane) was added to a stirred solution of diisopropylamine (1.96 g, 19.3 mM) in 60 mL of dry THF at -78°C. The reaction mixture was allowed to warm to 25°C and stirred for an additional 0.5 h and cooled to -78°C. δ -Valerolactone (2.00 g, 20 mM) in 50 mL of dry THF was added over an hour to the cold solution and stirred for another 0.5 h. Phenylselenenyl bromide (PhSeBr) in 7 mL of dry THF was added rapidly to the cold stirred enolate solution (immediate discoloration) and the cold reaction mixture was diluted with Et₂O. The ether solution was washed with 10% HCl, saturated NaHCO₃ and saturated NaCl. The organic layer was dried (MgSO₄) and concentrated in vacuo. The crude material (1.7 g) was dissolved in 20 mL of THF and 0.5 mL AcOH at 0°C. Hydrogen peroxide (30 mL, 30%) was added to the cold solution over 0.5 h and then stirred for an additional 0.5 h. The reaction mixture was poured into cold saturated NaHCO₃ and extracted with Et₂O. The organic layer was washed with H₂O, saturated NaCl, dried (MgSO₄) and the solvent removed in vacuo. Vacuum distillation afforded a colorless liquid (0.56 g, 25%): b.p. 54-66°C/0.4 mm; ¹H NMR (CCl₄) δ 1.85 (s, 3H, CH₃), 2.50=2.25 (m, 2H), 4.30 (t, 2H), 6.53 (m, 1H); IR (film) $\nu_{C=O}$ 1703 cm⁻¹; MS (70 eV) m/e (rel. abundance) 112 (67), 94 (11), 82 (62), 67 (41), 66 (11), 55 (18), 54 (100), 53 (37), 43 (16), 41 (24), 39 (94).

Anal. Calcd for C₆H₈O₂: C, 64.27; H, 7.19. Found: C, 63.88; H, 7.38.

1-Oxa-[4.4.0^{1,6}]bicyclodecene-2-one. Peroxide 3 (10 mg, 0.05 mM) was added to a solution of p-toluenesulfonic acid (8 mg) in 10 mL of benzene and heated at reflux for 27 h. The reaction mixture was diluted with Et₂O, washed with 10% NaHCO₃, saturated NaCl, and dried (MgSO₄). The solvent was removed in vacuo and the crude lactone was purified by column chromatography (silica gel, Et₂O)

to yield 4 mg (52%) of lactone: ^1H NMR (CCl_4) δ 1.65 (m, 4H), 2.20 (m, 6H), 4.25 (t, 2H); IR (CCl_4) $\nu_{\text{C=O}}$ 1720 cm^{-1} ; MS m/e (rel. abundance) 152 (67), 134 (19), 122 (10), 107 (62), 106 (23), 93 (22), 91 (42), 80 (12), 79 (100), 78 (10), 77 (28), 67 (13), 65 (13).

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_2$: 152.0837. Found: 152.0828.

Acknowledgement: This work was supported by the Office of Naval Research and by the National Science Foundation.

Table 1: Rate of Reaction of Peroxide 3 in Benzonitrile Containing $10^{-2}M$ Acetic Acid.

Activator	Temp. °C	k_1 , S^{-1} ^a	k_{cat} , $M^{-1}S^{-1}$ ^a
DPEA	149	4.7×10^{-3}	9.7
DPEA	144	7.8×10^{-3}	8.8
DPEA	140	1.8×10^{-3}	7.6
DPEA	135	1.4×10^{-3}	5.2
DPEA	130	7.8×10^{-4}	4.1
DPEA	120	7×10^{-5}	2.5
Perylene	130	1.1×10^{-3}	60
DPA	130	1.0×10^{-3}	1.7

a. The average deviation of replicate determinations of the first order rate constants used to determine k_1 and k_{cat} is 10% of the measured value.

References and Notes

1. Schuster, G. B.; Schmidt, S. P., Adv. Phys. Org. Chem., 1982, 18, 187.
2. Schuster, G. B., Accounts Chem. Res., 1979, 12, 366.
3. Silbert, S. S. in "Organic Peroxides" V. II, Swern, D., editor, Wiley-Interscience, N.Y., 1971, p. 755.
4. Rauhut, M. M., Accounts Chem. Res., 1969, 2, 80.
5. White, E. H.; Roswell, D. F., Accounts Chem. Res., 1970, 3, 541.
6. Adam, W.; Rucktäschel, R. J. Am. Chem. Soc., 1971, 93, 557.
7. Adam, W.; Rucktäschel, R. J. Org. Chem., 1978, 43, 3886.
8. Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriguez, O.; Rucktäschel, R. J. Am. Chem. Soc., 1972, 94, 1365.
9. Adam, W.; Liu, J.-C.; Rodriguez, O. J. Org. Chem., 1973, 38, 2269.
10. Hiatt, R.; in "Organic Peroxides" Vol. II, Swern, D.; editor, Wiley-Interscience, N. Y., 1971, p. 812.
11. Benson, S. W.; "Thermochemical Kinetics", (2nd edn). Wiley, N.Y., 1976.
12. Wilt, J. W.; in "Free Radicals", Vol. I, Kochi, J. K.; editor, Wiley, N.Y., Chapter 8.
13. Kochi, J. K., Krusic, P. J.; Eaton, D. R. J. Am. Chem. Soc., 1969, 91, 1877.
Kochi, J. K., Krusic, P. J.; Eaton, D. R. ibid. 1969, 91, 1879.
14. Griller, D.; Ingold, K. U. Accounts Chem. Res. 1980, 13, 317.
15. Krapcho, A. P.; Kashdan, D. S.; Tetrahedron Lett., 1975, 707.
16. Greene, F. D.; J. Am. Chem. Soc., 1956, 78, 2246.
17. Ryu, I.; Murai, S.; Sonoda, N. Tetrahedron Lett., 1977, 4611.
18. Greatorex, D.; Kemp, T. J. Trans. Faraday Soc., 1971, 67, 1576.
19. Pryor, W. A.; Smith, K. Int. J. Chem. Kinet., 1971, 3, 387.
20. Scandola, F.; Balzani, V.; Schuster, G. B. J. Am. Chem. Soc., 1981, 103, 2519.
21. Wilson, T.; Schaap, A. P. J. Am. Chem. Soc., 1971, 93, 4126.
22. Vassil'ev, R. F. Prog. React. Kinet., 1967, 4, 305.

Captions for Figures:

Figure 1. The effect of DPEA concentration on the observed first-order rate constant for reaction of peroxide 3 in benzonitrile containing $1 \times 10^{-2} \text{M}$ acetic acid at 130°C .

Figure 2. The effect of temperature on the initial chemiluminescence intensity from peroxide 3 and DPEA in benzonitrile solution.

Figure 3. Correlation of the initial chemiluminescence intensity from peroxide 3 and various activators, corrected for fluorescence quantum yield, photomultiplier tube and monochromator spectral response, with the one electron oxidation potential of the activator. Activator 1 is DPA, 2 is DPEA, 3 is perylene, and 4 is 5,10-diphenylethynyltetracene.

Figure 4. Stern-Volmer plot for the quenching of the DPEA activated chemiluminescence of peroxide 3 in benzonitrile with acetic acid.

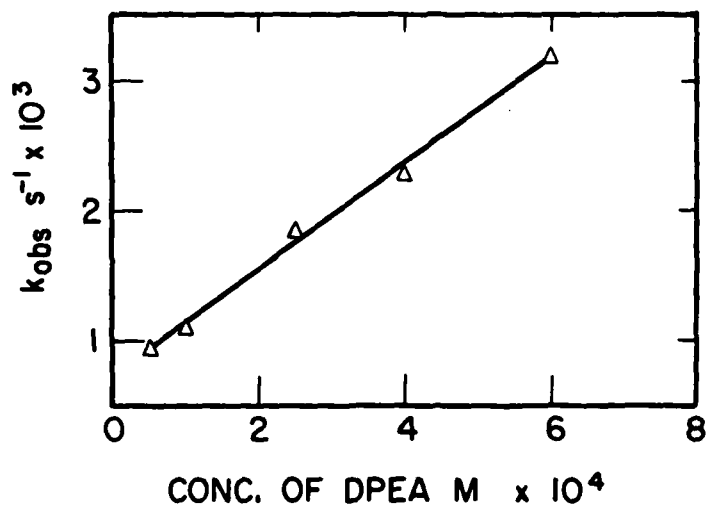


FIGURE 1

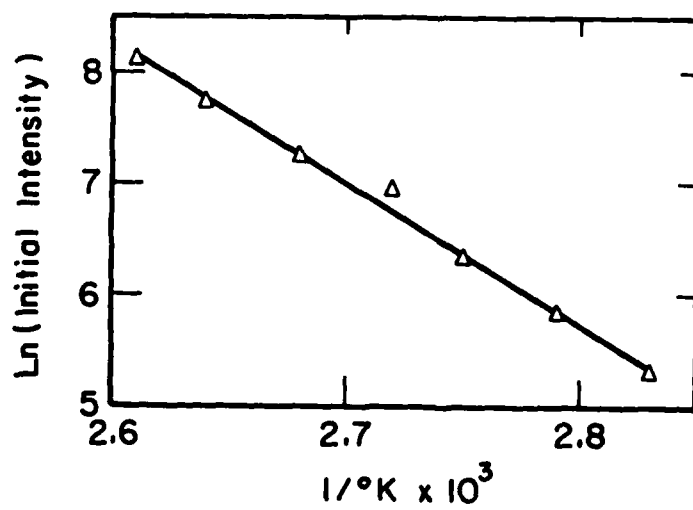


FIGURE 2

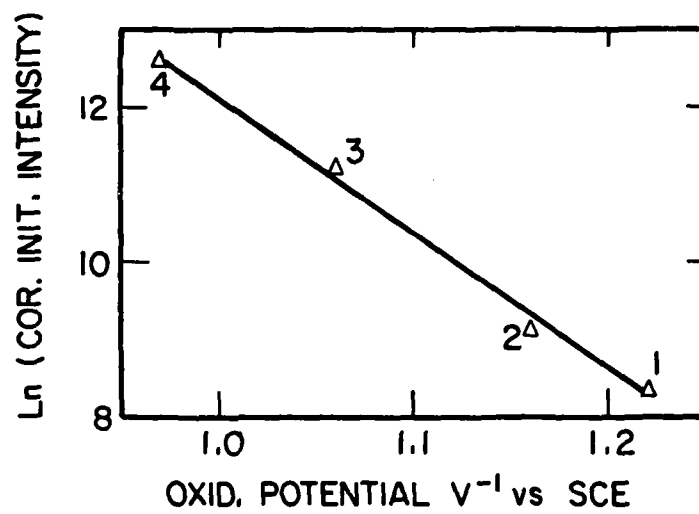


FIGURE 3

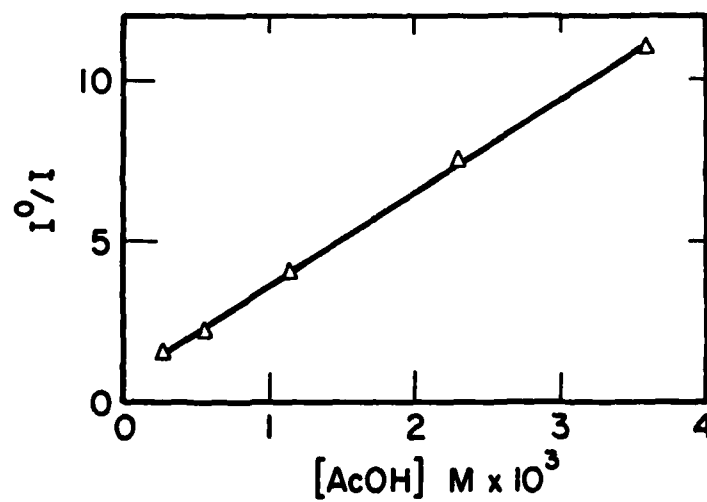


FIGURE 4

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

SP472-3/A3

472:GAN:716:ddc
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. M. A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1	Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1	Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. D. Haarer IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1	Dr. William M. Jackson Department of Chemistry Howard University Washington, DC 20059	1
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1	Dr. George E. Walraffen Department of Chemistry Howard University Washington, DC 20059	1
Dr. M. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1		

ATE
LMED
8